

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 866 099 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
23.09.1998 Bulletin 1998/39

(51) Int. Cl.⁶: **C08L 83/04**

(21) Application number: **98105081.8**

(22) Date of filing: **20.03.1998**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **21.03.1997 US 41340 P**
10.06.1997 US 872518

(71) Applicant:
DOW CORNING CORPORATION
Midland, Michigan 48686-0994 (US)

(72) Inventors:
• **Beljanski, Philip David**
Midland, Michigan 48640 (US)
• **Lower, Loren Dale**
Midland, Michigan 48642 (US)

(74) Representative:
Spott, Gottfried, Dr. et al
Patentanwälte
Spott, Weinmiller & Partner
Sendlinger-Tor-Platz 11
80336 München (DE)

(54) **Oil resistant silicone sealants**

(57) The invention relates to a RTV silicone composition having increased hot oil resistance upon curing. The RTV silicone composition comprises a polydiorganosiloxane, an acyloxy-functional crosslinker, a metal salt of a carboxylic acid catalyst, a filler, and a metal acetylacetonate. In a preferred embodiment a metal oxide is also added.

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Description

The use of room temperature vulcanizing (RTV) silicone sealants for creating formed-in-place gaskets is well known in both original equipment manufacture and in repair and maintenance. A problem with certain conventional silicone sealants is their tendency in the presence of hot oil to lose structural integrity leading to seal failure. Therefore, it is desirable to have silicone sealants providing increased oil resistance as demonstrated by increased tensile strength in the presence of hot oil.

The prior art is represented by U.S. Patent No. 4,123,472; U.S. Patent No. 4,680,363; U.S. Patent No. 4,833,037; U.S. Patent No. 4,257,932 and U.S. Patent No. 4,797,462.

The present inventors have unexpectedly determined that the addition of a metal acetylacetonate, preferably along with a metal oxide, to a RTV silicone composition comprising a polydiorganosiloxane, acyloxy-functional crosslinker, filler, and tin catalyst results in a cured composition having increased hot oil resistance. In addition, these compositions may find use when cured as sealants, adhesives, gaskets, coatings, molding and potting compounds and gels.

The RTV silicone composition which is curable in the presence of moisture comprises a polydiorganosiloxane, an acyloxy-functional crosslinker, a metal salt of a carboxylic acid catalyst, a filler, and a metal acetylacetonate.

This invention is a RTV silicone composition which is curable in the presence of moisture and has increased hot oil resistance upon curing comprising:

(A) 100 parts by weight of a polydiorganosiloxane in which the terminal groups are selected from silanol and triorganosilyl groups, provided at least 60 mole percent of the terminal groups are silanol groups;

(B) 1 to 15 parts by weight of an acyloxy-functional crosslinking agent described by the formula $R_mSi(OCOR')_{4-m}$ where R is a monovalent hydrocarbon radical selected from 1 to 12 carbon atoms, each R' is an independently selected monovalent hydrocarbon radical from 1 to 12 carbon atoms and m is 0 or 1;

(C) 0.001 to 1 part by weight of a metal salt of a carboxylic acid catalyst;

(D) 5 to 150 parts by weight of a filler; and

(E) an effective amount of a metal acetylacetonate.

Component (A) is a polydiorganosiloxane having terminal groups selected from silanol and triorganosilyl groups, provided at least 60 mole percent of the terminal groups are silanol groups. The polydiorganosiloxane may be one type of polymer or a mixture of different polymers. The polydiorganosiloxanes may have a linear structure and may be homopolymers or copolymers. In addition, the organic groups linked to any particular silicon atom may be the same or different. The organic groups of the polydiorganosiloxane can include any monovalent hydrocarbon group or any monovalent halohydrocarbon group comprising 1 to 18 carbon atoms. Preferred organic groups are methyl, ethyl, propyl, phenyl, vinyl and 3,3,3-trifluoropropyl, with methyl being most preferred.

The terminal groups of the polydiorganosiloxane are selected from silanol and triorganosilyl groups. The organic substituent of the triorganosilyl groups can include any monovalent hydrocarbon group or any monovalent halohydrocarbon group comprising 1 to 18 carbon atoms. The preferred organic substituent of the triorganosilyl groups are methyl, ethyl, propyl, phenyl, vinyl, and 3,3,3-trifluoropropyl, with methyl being most preferred.

Although the terminal groups are selected from silanol and triorganosilyl groups, it is required that at least 60 mole percent of the terminal groups be silanol groups in order to obtain the desired properties of the composition when cured. Preferably, 80 to 100 mole percent of the terminal groups of the polydiorganosiloxane are silanol groups.

The viscosity of the polydiorganosiloxane may be from 1 to 150 Pa · s at 25°C. The preferred viscosity of the polydiorganosiloxane is from 5 to 100 Pa · s at 25°C.

The methods of manufacture of the silanol terminated polydiorganosiloxanes are well known in the art. One common method is based upon the hydrolysis of diorganodichlorosilane, the separation of a diorganotetrasiloxane cyclic material from the hydrolysis mixture, and the subsequent polymerization of the cyclic material to the polydiorganosiloxane through the use of an alkaline catalyst. The triorganosilyl terminated polydiorganosiloxanes are also prepared by known methods described in U.S. Patent No. 3,274,145.

Component (B) is an acyloxy-functional crosslinking agent described by the formula $R_mSi(OCOR')_{4-m}$ where R is a monovalent hydrocarbon radical selected from 1 to 12 carbon atoms, each R' is an independently selected monovalent hydrocarbon radical from 1 to 12 carbon atoms and m is 0 or 1.

The monovalent hydrocarbon radicals represented by R may be linear or branched and can include alkyl radicals such as methyl, ethyl, isopropyl or hexyl; alkenyl radicals such as vinyl, allyl or hexenyl; alkynyl radicals such as propargyl; cycloaliphatic radicals such as cyclopentyl, cyclohexyl or cyclohexenyl; aromatic radicals such as phenyl or tolyl; and aralkyl radicals such as benzyl or beta-phenylethyl. R is preferably methyl or ethyl.

Each R' is an independently selected monovalent hydrocarbon radical from 1 to 12 carbon atoms. Examples of R' include those provided for R. R' is preferably methyl or ethyl, with methyl being most preferred.

The acyloxy-functional crosslinker may have trifunctionality, as occurs when m is 1 or tetrafunctionality, as occurs

when m is 0. It is preferred that m be 1.

Examples of preferred acyloxy-functional crosslinkers include methyltriacetoxysilane, ethyltriacetoxysilane, methyltris-benzoxysilane, vinyltriacetoxysilane and methyl-tris-2-ethylhexanoxy silane.

The acyloxy-functional crosslinker can be present in the present composition in amounts from 1 to 15 parts by weight based on 100 parts by weight of the polydiorganosiloxane, and preferably from 2 to 10 parts by weight on the same basis. The acyloxy-functional crosslinker may be added as a single species or as a mixture of two or more species.

Component (C) is a metal salt of a carboxylic acid catalyst. The metal component of the catalyst is preferably tin, but may be lead, chromium, antimony, iron, cadmium, barium, titanium, bismuth or magnesium. Examples of suitable metal salts of carboxylic acids include tin naphthenate, lead octoate, tin octoate, iron stearate, tin oleate, dibutyltindilaurate, dibutyltindiacetate, dibutyl tin oxide, and dimethyl tin bis-neodecanoate. Preferred catalysts are dibutyltindilaurate, dibutyltindiacetate, and dimethyl tin bis-neodecanoate. The most preferred catalysts are dibutyltindilaurate and dibutyltindiacetate.

The catalyst can be present in the present composition in amounts from 0.001 to 1 part by weight based on 100 parts by weight of the polydiorganosiloxane, and preferably from 0.01 to 0.3 part by weight on the same basis. It is most preferred to have 0.01 to 0.2 part by weight catalyst present in the composition on the same basis. The catalyst may be added as a single species or as a mixture of two or more species.

In order to obtain the desired physical properties of the present composition when cured, a filler (Component (D)) is added to the composition. This filler may include reinforcing fillers, semi-reinforcing fillers, or non-reinforcing fillers also called extending fillers, or any combination thereof. One or more of each type of filler is also acceptable.

Reinforcing fillers include any finely divided form of silica which can be prepared by precipitation or a pyrogenic process and may be treated or untreated. Generally, methods of treating the silica can include mixing the silica with polycyclosiloxane such as disclosed in U.S. Patent No. 2,938,009 or U.S. Patent No. 3,004,859 or silazanes as disclosed in U.S. Patent 3,635,743. The treating agents may also include liquid hydroxyl-terminated polydiorganosiloxanes which can contain an average of about 2 to 20 repeating units and can contain at least one alkenyl unit. The treating agent may also be an alkylhalosilane, such as dimethyldichlorosilane or an alkoxysilane. Carbon black is also useful as a reinforcing filler in this invention. Semi-reinforcing fillers include barium sulfate and crystalline silica. Non-reinforcing or extending fillers include glass spheres, wollastonite, diatomaceous earths, clay and talc. The preferred fillers are untreated fumed silica and treated fumed silica.

The filler can be present in the present composition in amounts from 5 to 150 parts by weight based on 100 parts by weight of the polydiorganosiloxane, and preferably, from 5 to 30 parts by weight on the same basis. The filler may be added as a single species or as a mixture of two or more species.

Component (E) is a metal acetylacetonate. The inventors have unexpectedly determined that the addition of a metal acetylacetonate to an RTV silicone composition provides the composition upon curing with increased hot oil resistance.

The metal portion of the metal acetylacetonate is preferably copper, iron or zirconium, with copper being most preferable, but may be selected from copper, chromium, iron, aluminum, zinc, titanium and zirconium. Examples of Component (E) include copper II acetylacetonate, ferric acetylacetonate, chromium III acetylacetonate and zinc acetylacetonate.

An effective amount of the metal acetylacetonate is an amount which provides increased hot oil resistance to the RTV silicone composition upon curing. Typically, 0.01 to 5 parts by weight metal acetylacetonate based on 100 parts by weight of the polydiorganosiloxane is effective. It is preferable to add 0.05 to 1.5 parts by weight metal acetylacetonate on the same basis, with 0.1 to 0.6 part by weight metal acetylacetonate on the same basis being most preferred. The metal acetylacetonate may be added as a single species or as a mixture of two or more species.

In a preferred embodiment Component (F), a metal oxide, is also added to the RTV silicone composition. The metal portion of the metal oxide is most preferably calcium, but may also be selected from calcium, zinc, magnesium, aluminum, zirconium, barium, titanium, strontium and copper. Examples of Component (F) include calcium oxide, zinc oxide, magnesium oxide, aluminum oxide, zirconium oxide, barium oxide, titanium IV dioxide and copper II oxide.

The metal oxide can be present in the present composition in amounts from 0.01 to 10 parts by weight based on 100 parts by weight of the polydiorganosiloxane. It is preferable to add from 0.01 to 1.5 parts by weight on the same basis and, most preferably, from 0.01 to 1 part by weight on the same basis. The metal oxide may be added as a single species or as a mixture of two or more species.

In preferred embodiments, the present compositions can also optionally include up to 2 parts by weight of an adhesion promoter based on 100 parts by weight of the polydiorganosiloxane. Examples of useful adhesion promoters include ethylpolysilicate and glycidoxypolytrimethoxysilane.

In addition to the above ingredients, the present composition may include additives which impart or enhance certain properties of the cured composition or facilitate processing of the curable composition. Typical additives include plasticizers, functional and non-functional diluents, pigments, dyes, heat and/or ultraviolet light stabilizers, flame-retard-

ant agents, thickeners, rheology modifiers, and preservatives. The effect of any such additives should be evaluated as to their result and impact on other properties of the composition.

The RTV silicone composition of this invention may be prepared by mixing all the ingredients together in amounts as specified to provide a composition which is stable in the absence of moisture and which cures to an elastomeric material when exposed to moisture.

These compositions are preferably prepared by mixing the ingredients under anhydrous conditions. This means that the amounts of moisture or water in the ingredients used should be minimized and the conditions of mixing should minimize the amounts of moisture or water allowed into the system. Excess moisture or water may have deleterious effects on the composition, such as causing curing in the storage package or reduced cured properties.

The present compositions may be prepared as either a one package system or a two (or multi) package system. With a one package system, all the ingredients are mixed together and stored in an anhydrous state. With a two or multi package system the ingredients may be stored separately and then mixed prior to use. It is often convenient to form a "base" blend comprising a polydiorganosiloxane, a filler and, if needed, a plasticizer (I). Another blend comprising curing agents such as the crosslinker and catalyst may also be mixed together (II) and still another blend comprising additional ingredients including Components (E) and (F) may also be mixed together (III). As described above, the components comprising (I), (II) and (III) may be mixed together or separately. If mixed and stored together a one part sealant results. Obviously a two or multi package system is possible if (I), (II), and (III) are mixed and packaged separately. It is also possible to mix and store two of the components together, i.e., (I) and (III) and later mix in (II). In a preferred embodiment of the present invention, it is preferred to mix and store (I) and (II) together and then later mix in (III) as required.

The present RTV silicone compositions may be used as gasket materials for sealing gaps or seams in a given substrate or for sealing between substrates. Due to the oil resistance of the present RTV silicone compositions when cured these compositions are preferably used for sealing gaps or substrates having surfaces exposed to oil or hot oil. However, these RTV silicone compositions may also be used to seal gaps or substrates which may not have surfaces exposed to oil or hot oil.

A method for sealing using the present composition comprises (i) providing at least two substrates having a plurality of surfaces; (ii) applying a layer of a RTV silicone composition which is curable in the presence of moisture, to at least a portion of at least one of the surfaces of at least one of the substrates, the RTV silicone composition comprising Components (A)-(E) and preferably also Component (F), as described above; (iii) bringing at least two of the substrates, where at least one of the substrates has the RTV silicone composition applied thereto, into proximity so as to form a gasket of the RTV silicone composition therebetween; and (iv) exposing the gasket of step (iii) to moisture to effect curing of the RTV silicone composition.

The substrates useful for this preferred embodiment can be metal materials, composites or certain plastic materials. Preferably the substrates are metal materials.

The following examples are presented for illustrative purposes and should not be construed as limiting the invention which is delineated in the claims.

In the following examples, unless otherwise noted, the compositions were mixed at $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $50\% \pm 5\%$ relative humidity; cast, and then cured for 7 days at $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $50\% \pm 5\%$ relative humidity before oil immersion testing. The cured samples were then immersed in oil for 14 days at 150°C per ASTM D471 except the samples were cooled to $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ in the test fluid rather than in a cooling fluid. The oil used for immersion testing was Goodwrench 5W30 SAE SH/SG. The durometer (Shore A) results provided in each table were obtained using the method described in ASTM D2240 with the following exceptions: 2.54 cm x 1.91 cm tabs having a thickness of 0.64 cm were tested and an average of 5 readings was reported. The tensile, 100% modulus, and elongation results provided in each table were obtained using the method described in ASTM D412 with each tensile, 100% modulus, and elongation value reported as the average of 3 samples. Adhesion testing was conducted according to ASTM D903 with the following exceptions: 1) the speed of testing was 5.08 cm/min., 2) substrates were cleaned with MIBK (methylisobutylketone) followed by an acetone rinse and 3) the flexible substrate was 1.27 cm wide. Volume swell % results were obtained using the method described in ASTM 471. Also, as used herein "part" or "parts" are by weight and "AcAc" refers to acetylacetonate.

Prior to use, the metal oxide powder was dried at 105°C . for a minimum of 2 hours. All metal oxides used in the examples with the exception of copper II oxide were obtained from Fisher Scientific (Pittsburgh, PA). Copper II oxide was obtained from Aldrich Chemical (Milwaukee, WI). Copper II AcAc was obtained from Acros Organics (Pittsburgh, PA) and Aldrich Chemical. Chromium III AcAc, Iron III AcAc and Aluminum AcAc were obtained from Acros Organics. Zinc AcAc Hydrate, Titanium IV Oxide AcAc and Zirconium AcAc were obtained from Aldrich Chemical. The fumed silica was obtained from Cabot Corp (Tuscola, IL). The dibutyl tin diacetate was obtained from Atochem Corporation (Philadelphia, PA). The silane and siloxane compounds were obtained from Dow Corning Corporation (Midland, MI). Ethylpolysilicate was obtained from Huls of America, Inc. (Piscataway, NJ).

Example 1

Formulations were prepared as shown in Table 1.1. Ingredients numbered as 1, 2, 3 and 8 were combined with a compounder at approximately 70°C., packaged into cartridges and then deaired. Ingredients numbered 4, 5, 6, 7 and 9 were mixed together and then injected into and mixed with the mixture of ingredients 1, 2, 3 and 8 using a Semco mixer (Model 388, Products Research and Chemical Corp, Glendale, CA). Samples were cast, cured and then tested in hot oil. Formulations 1A and 1C are controls while Formulations 1B and 1D have added copper acetylacetonate and calcium oxide. The post oil immersion tensile strength improved from less than 0.09 N/mm² without the additives to greater than 0.75 N/mm² with the additives. The results are provided in Tables 1.2(a) and 1.2(b).

Table 1.1

| Formulations | | | | | |
|--------------|---------------------------------------------------------------------------------------|-----------|----------|-----------|----------|
| | Component (parts) | Form. 1A* | Form. 1B | Form. 1C* | Form. 1D |
| 1. | 17.5 Pa • s, 85% silanol terminated and 15% trimethyl terminated polydimethylsiloxane | 100.00 | 100.00 | 100.00 | 100.00 |
| 2. | Untreated fumed silica having a surface area of approximately 200 m ² /g | 13.86 | 13.79 | 12.38 | 11.69 |
| 3. | Mixture of methyl(~45%) and ethyl(~55%) triacetoxysilane | 6.19 | 6.19 | 5.55 | 5.23 |
| 4. | 0.1 Pa • s Trimethyl Endblocked Polydimethylsiloxane | 4.80 | 4.80 | 4.72 | 4.68 |
| 5. | Approximately 0.075 Pa • s hydroxy-terminated polydimethylsiloxane | 2.40 | 2.4 | 2.36 | 2.34 |
| 6. | Copper acetylacetonate | 0.00 | 0.24 | 0.00 | 0.24 |
| 7. | Calcium Oxide | 0.00 | 0.36 | 0.00 | 0.35 |
| 8. | Dibutyl tin diacetate | 0.03 | 0.03 | 0.03 | 0.03 |
| 9. | Blue Silicone Paste** | 0.64 | 0.64 | 0.63 | 0.63 |

* Formulations 1A and 1C are the controls, with no additives included.

** Ferro SV1232, Ferro Corp. (Edison, NJ)

Table 1.2(a)

| Initial Results Prior to Oil Immersion | | | | |
|----------------------------------------|-----------|----------|-----------|---------|
| | Form. 1A* | Form. 1B | Form. 1C* | Form 1D |
| Durometer, Shore A | 23 | 28 | 28 | 23 |
| Tensile Strength, N/mm ² | 1.48 | 1.69 | 2.16 | 1.48 |
| Elongation, % | 349 | 366 | 460 | 349 |
| Modulus @ 100%, N/mm ² | 0.50 | 0.54 | 0.56 | 0.50 |

* Formulations 1A and 1C are the controls, with no additives included.

Table 1.2(b)

| 5W30 Oil Immersion Results | | | | |
|-------------------------------------|-----------|----------|-----------|---------|
| | Form. 1A* | Form. 1B | Form. 1C* | Form 1D |
| Durometer, Shore A | 0 | 6 | 0 | 4 |
| Tensile Strength, N/mm ² | 0.09 | 0.75 | 0.04 | 0.71 |
| Elongation, % | 233 | 442 | 26 | 502 |
| Modulus @ 100%, N/mm ² | 0.08 | 0.28 | N/A | 0.21 |
| Volume Swell % | 55 | 51 | 35 | 52 |

* Formulations 1A and 1C are the controls, with no additives included.

Example 2

The ingredients listed in Table 2.1 were mixed and tested as described in Example 1. Ingredients numbered as 1, 2, 3 and 7 were combined with a compounder at approximately 70°C. The mixture was then pigmented by mixing in ingredient 8, packaged into cartridges and then deaired. Ingredients numbered 4, 5 and 6 were mixed together and then injected into and mixed with the mixture of ingredients 1, 2, 3, 7 and 8 using a Semco mixer. The post oil immersion tensile strength was improved with the addition of the copper AcAc or calcium oxide added individually, however, the combined effect is greater than either with copper AcAc or calcium oxide added individually. The results are provided in Tables 2.2(a) and 2.2(b).

Table 2.1

| Formulations | | | | | |
|--------------|---------------------------------------------------------------------------------------|-----------|----------|----------|----------|
| | Component (parts) | Form. 2A* | Form. 2B | Form. 2C | Form. 2D |
| 1. | 17.5 Pa · s, 85% silanol terminated and 15% trimethyl terminated polydimethylsiloxane | 100.00 | 100.00 | 100.00 | 100.00 |
| 2. | Untreated fumed silica having a surface area of approximately 200 m ² /g | 13.36 | 13.36 | 13.36 | 13.86 |
| 3. | Mixture of methyl(~45%) and ethyl(~55%) triacetoxysilane | 5.97 | 5.97 | 5.97 | 6.19 |
| 4. | 12 Pa · s Trimethyl Endblocked Polydimethylsiloxane | 1.98 | 1.98 | 1.98 | 2.05 |
| 5. | Copper acetylacetonate | 0.00 | 0.31 | 0.00 | 0.64 |
| 6. | Calcium Oxide | 0.00 | 0.00 | 0.62 | 0.64 |
| 7. | Dibutyl tin diacetate | 0.02 | 0.02 | 0.02 | 0.03 |
| 8. | Black Pigment** | 2.48 | 2.48 | 2.48 | 2.57 |

* Formulation 2A is the control, with no additives included.

** Paste of LV1011 Lampblack Powder, Harcross Pigments (Fairview Heights, IL)

Table 2.2(a)

| Initial Results Prior to Oil Immersion | | | | |
|----------------------------------------|-----------|----------|----------|----------|
| | Form. 2A* | Form. 2B | Form. 2C | Form. 2D |
| Durometer, Shore A | 25 | 26 | 26 | 27 |
| Tensile Strength, N/mm ² | 2.02 | 1.73 | 2.01 | 1.70 |
| Elongation, % | 473 | 426 | 469 | 405 |
| Modulus @ 100%, N/mm ² | 0.47 | 0.49 | 0.48 | 0.50 |

* Formulation 2A is the control, with no additives included.

Table 2.2(b)

| 5W30 Oil Immersion Results | | | | |
|-------------------------------------|-----------|----------|----------|----------|
| | Form. 2A* | Form. 2B | Form. 2C | Form. 2D |
| Durometer, Shore A | 0 | 0 | 0 | 6 |
| Tensile Strength, N/mm ² | 0.00 | 0.28 | 0.42 | 1.05 |
| Elongation, % | 0 | 849 | 589 | 574 |
| Modulus @ 100%, N/mm ² | 0.00 | 0.08 | 0.16 | 0.26 |
| Volume Swell % | N/A | 57 | 58 | 54 |

* Formulation 2A is the control, with no additives included.

Example 3

The ingredients listed in Table 3.1 were mixed and tested as described in Example 1. Ingredients numbered as 1, 2, 3 and 7 were combined with a compounder at approximately 70°C., packaged into cartridges and then deaired. Ingredients numbered 4, 5 and 6 were mixed together and then injected into and mixed with the mixture of ingredients 1, 2, 3 and 7 using a Semco mixer. In this example, different amounts of the copper AcAc and calcium oxide were used individually (Tables 3.1(a) and 3.1(b) respectively) and in combination (Table 3.1(c)). The results are provided in Tables 3.2(a) and 3.2(b).

Table 3.1(a)

| Addition of Copper Acetylacetonate Only | | | | | | |
|-----------------------------------------|---------------------------------------------------------------------------------------|---------|---------|---------|---------|---------|
| | Component (parts) | 3A | 3B | 3C | 3D | 3E |
| 1. | 17.5 Pa · s, 85% silanol terminated and 15% trimethyl terminated polydimethylsiloxane | 100.0 0 | 100.0 0 | 100.0 0 | 100.0 0 | 100.0 0 |
| 2. | Untreated fumed silica having a surface area of approximately 200 m ² /g | 22.21 | 22.21 | 22.21 | 22.21 | 22.21 |
| 3. | Mixture of methyl(~45%) and ethyl(~55%) triacetoxysilane | 9.15 | 9.15 | 9.15 | 9.15 | 9.15 |
| 4. | 12 Pa · s Trimethyl Endblocked Polydimethylsiloxane | 1.97 | 1.97 | 1.97 | 1.97 | 1.97 |
| 5. | Copper acetylacetonate | 0.32 | 0.52 | 0.99 | 1.31 | 1.97 |
| 6. | Calcium Oxide | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7. | Dibutyl tin diacetate | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |

Table 3.1(b)

| Addition of Calcium Oxide Only | | | | | |
|--------------------------------|---------------------------------------------------------------------------------------|---------|---------|---------|---------|
| | Component (parts) | 3F | 3G | 3H | 3I |
| 1. | 17.5 Pa • s, 85% silanol terminated and 15% trimethyl terminated polydimethylsiloxane | 100.0 0 | 100.0 0 | 100.0 0 | 100.0 0 |
| 2. | Untreated fumed silica having a surface area of approximately 200 m ² /g | 22.21 | 22.21 | 22.21 | 22.21 |
| 3. | Mixture of methyl(~45%) and ethyl(~55%) triacetoxysilane | 9.15 | 9.15 | 9.15 | 9.15 |
| 4. | 12 Pa • s Trimethyl Endblocked Polydimethylsiloxane | 2.10 | 2.10 | 2.10 | 2.10 |
| 5. | Copper acetylacetonate | 0.00 | 0.00 | 0.00 | 0.00 |
| 6. | Calcium Oxide | 0.33 | 0.65 | 0.98 | 1.32 |
| 7. | Dibutyl tin diacetate | 0.05 | 0.05 | 0.05 | 0.05 |

Table 3.1(c)

| Addition of Copper Acetylacetonate and Calcium Oxide | | | |
|------------------------------------------------------|---------------------------------------------------------------------------------------|--------|--------|
| | Component (parts) | 3J | 3K |
| 1. | 17.5 Pa • s, 85% silanol terminated and 15% trimethyl terminated polydimethylsiloxane | 100.00 | 100.00 |
| 2. | Untreated fumed silica having a surface area of approximately 200 m ² /g | 22.21 | 22.21 |
| 3. | Mixture of methyl(~45%) and ethyl(~55%) triacetoxysilane | 9.15 | 9.15 |
| 4. | 12 Pa • s Trimethyl Endblocked Polydimethylsiloxane | 2.10 | 2.63 |
| 5. | Copper acetylacetonate | 0.33 | 0.66 |
| 6. | Calcium Oxide | 0.98 | 0.66 |
| 7. | Dibutyl tin diacetate | 0.05 | 0.05 |

Table 3.2(a)

| Initial Results Prior to Oil Immersion | | | | |
|----------------------------------------|-------------------|---------------------------|--------------|--------------------------------|
| Formulation | Durometer Shore A | Tensile N/mm ² | Elongation % | 100% Modulus N/mm ² |
| 3A | 46 | 2.47 | 240 | 1.30 |
| 3B | 46 | 2.70 | 269 | 1.27 |
| 3C | 48 | 2.79 | 280 | 1.27 |
| 3D | 49 | 2.42 | 239 | 1.28 |
| 3E | 49 | 2.43 | 244 | 1.28 |
| 3F | 45 | 2.73 | 306 | 1.14 |

Table 3.2(a) (continued)

| Initial Results Prior to Oil Immersion | | | | |
|----------------------------------------|-------------------|---------------------------|--------------|--------------------------------|
| Formulation | Durometer Shore A | Tensile N/mm ² | Elongation % | 100% Modulus N/mm ² |
| 3G | 46 | 2.68 | 299 | 1.14 |
| 3H | 44 | 2.83 | 318 | 1.13 |
| 3I | 43 | 2.97 | 328 | 1.12 |
| | | | | |
| 3J | 44 | 2.73 | 283 | 1.21 |
| 3K | 47 | 2.47 | 251 | 1.27 |

Table 3.2(b)

| 5W30 Oil Immersion Results | | | | | |
|----------------------------|-------------------|---------------------------|--------------|--------------------------------|----------------|
| Formulation | Durometer Shore A | Tensile N/mm ² | Elongation % | 100% Modulus N/mm ² | Volume Swell % |
| 3A | 13 | 0.88 | 354 | 0.42 | 36 |
| 3B | 15 | 0.92 | 294 | 0.49 | 35 |
| 3C | 17 | 1.14 | 329 | 0.53 | 35 |
| 3D | 15 | 1.05 | 311 | 0.52 | 35 |
| 3E | 14 | 0.96 | 305 | 0.5 | 35 |
| | | | | | |
| 3F | 14 | 0.72 | 260 | 0.45 | 37 |
| 3G | 17 | 1.07 | 271 | 0.61 | 37 |
| 3H | 18 | 1.32 | 317 | 0.59 | 37 |
| 3I | 19 | 1.27 | 266 | 0.59 | 34 |
| | | | | | |
| 3J | 22 | 1.45 | 290 | 0.68 | 32 |
| 3K | 23 | 1.50 | 282 | 0.74 | 29 |

Example 4

The ingredients listed in Table 4.1 were mixed and tested as described in Example 1. Ingredients numbered as 1, 2, 3 and 8 were combined with a compounder at approximately 70°C., packaged into cartridges and then deaired. Ingredients numbered 4, 5, 6, 7, 9 and 10 were mixed together and then injected into and mixed with the mixture of ingredients 1, 2, 3 and 8 using a Semco mixer. In this example, an adhesion promoter (10) was also added. The adhesion promoter did not result in degraded oil resistance. The results are provided in Tables 4.2(a) and 4.2(b).

Table 4.1

Formulations

| | Component (parts) | Form. 4A | Form. 4B | Form. 4C | Form. 4D |
|-----|---------------------------------------------------------------------------------------|----------|----------|----------|----------|
| 1. | 17.5 Pa · s, 85% silanol terminated and 15% trimethyl terminated polydimethylsiloxane | 100.00 | 100.00 | 100.00 | 100.00 |
| 2. | Untreated fumed silica having a surface area of approximately 200 m ² /g | 13.89 | 13.93 | 15.05 | 15.15 |
| 3. | Mixture of methyl(~45%) and ethyl(~55%) triacetoxysilane | 6.20 | 6.22 | 6.78 | 6.82 |
| 4. | 0.1 Pa · s Trimethyl Endblocked Polydimethylsiloxane | 4.81 | 4.83 | 2.09 | 2.11 |
| 5. | Approximately 0.075 Pa · s hydroxy-terminated polydimethylsiloxane | 2.41 | 2.41 | 2.45 | 2.46 |
| 6. | Copper acetylacetonate | 0.24 | 0.25 | 0.25 | 0.25 |
| 7. | Calcium Oxide | 0.36 | 0.36 | 0.37 | 0.37 |
| 8. | Dibutyl tin diacetate | 0.03 | 0.03 | 0.03 | 0.03 |
| 9. | Blue Silicone Paste* | 0.48 | 0.48 | 0.48 | 0.49 |
| 10. | Ethylpolysilicate | 0.64 | 1.29 | 0.65 | 1.32 |

* Ferro SV1232, Ferro Corp. (Edison, NJ)

Table 4.2(a)

Initial Results Prior to Oil Immersion

| | Form. 4A | Form. 4B | Form. 4C | Form. 4D |
|---------------------------------------------|-----------------|------------------|------------------|-------------------|
| Durometer, Shore A | 25 | 25 | 28 | 28 |
| Tensile Strength, N/mm ² | 1.70 | 1.95 | 2.01 | 2.13 |
| Elongation, % | 425 | 452 | 429 | 469 |
| Modulus @ 100%, N/mm ² | 0.48 | 0.44 | 0.52 | 0.52 |
| Adhesion to 1010 steel/aluminum, pli (N/mm) | 6/28 (1.05/4.9) | 14/32 (2.45/5.6) | 6/34 (1.05/5.95) | 22/38 (3.85/6.65) |

Table 4.2(b)

5W30 Oil Immersion Results

| | Form. 4A | Form. 4B | Form. 4C | Form. 4D |
|-------------------------------------|----------|----------|----------|----------|
| Durometer, Shore A | 3 | 4 | 5 | 6 |
| Tensile Strength, N/mm ² | 0.70 | 0.74 | 0.91 | 0.97 |
| Elongation, % | 572 | 557 | 560 | 583 |
| Modulus @ 100%, N/mm ² | 0.19 | 0.21 | 0.23 | 0.23 |
| Volume Swell % | 55 | 52 | 49 | 48 |

Example 5

The ingredients listed in Table 5.1 were mixed and tested as described in Example 1. Ingredients numbered as 1, 2, 3 and 8 were combined with a compounder at approximately 70°C., packaged into cartridges and then deaired. Ingredients numbered 4, 5, 6, 7, 9 and 10 were mixed together and then injected into and mixed with the mixture of ingredients 1, 2, 3 and 8 using a Semco mixer. In this 5.2(a)(1) and (b)(1). Each Form. 5B incorporates calcium oxide with a metal AcAc as described in the results Tables 5.2(a)(2) and (b)(2).

Table 5.1

| Formulations | | | |
|--------------|------------------------------------------------------------------------------------------------|----------|---------|
| | Components (parts) | Form. 5A | Form 5B |
| 1 | 17.5 Pa • s viscosity 85% silanol terminated and 15% trimethyl terminated polydimethylsiloxane | 100 | 100 |
| 2 | Untreated fumed silica having a surface area of approximately 200 m ² /g | 13.09 | 13.09 |
| 3 | Mixture of methyl(~45%) and ethyl(~55%) triacetoxysilane | 5.86 | 5.86 |
| 4 | 0.1 Pa s Trimethyl Endblocked Polydimethylsiloxane | 4.76 | 4.76 |
| 5 | Approximately 0.075 Pa • s viscosity hydroxy-terminated polydimethylsiloxane. | 2.38 | 2.38 |
| 6a | copper acetylacetonate | 0.24 | 0.0 |
| 6b | metal acetylacetonate (see Tables 5.2(a)(1) and (b)(1)) | 0.0 | 0.24 |
| 7a | calcium oxide | 0.0 | 0.36 |
| 7b | metal oxide (see Tables 5.2(a)(2) and (b)(2)) | 0.36 | 0.0 |
| 8 | Dibutyl tin diacetate | 0.03 | 0.03 |
| 9 | Blue Silicone Paste* | 0.44 | 0.44 |
| 10 | ethylpolysilicate | 0.59 | 0.59 |

* Ferro SV1232, Ferro Corp. (Edison, NJ)

Table 5.2(a)

| Initial Results Prior to Oil Immersion | | | | |
|-----------------------------------------------------------------|---------------------|---------------------------|-------------|--------------------------------|
| (1) Samples containing a Metal AcAc and CaO (Form.(B)) | | | | |
| Additive | Durometer (Shore A) | Tensile N/mm ² | Elongation% | 100% Modulus N/mm ² |
| Chromium III AcAc | 24.0 | 1.89 | 392 | 0.48 |
| Iron III AcAc | 28.0 | 1.64 | 348 | 0.56 |
| Aluminum AcAc | 29.0 | 1.44 | 333 | 0.55 |
| Zirconium AcAc | 30.0 | 1.59 | 289 | 0.63 |
| Zinc AcAc Hydrate | 26.0 | 1.53 | 347 | 0.52 |
| Titanium IV Oxide AcAc | 33.0 | 1.59 | 270 | 0.68 |
| (2) Samples containing Copper AcAc and a Metal Oxide (Form.(A)) | | | | |
| Additive | Durometer (Shore A) | Tensile N/mm ² | Elongation% | 100% Modulus N/mm ² |
| Zinc Oxide | 26.0 | 1.65 | 393 | 0.50 |
| Magnesium Oxide | 26.0 | 1.56 | 400 | 0.48 |
| Titanium Dioxide | 26.0 | 2.04 | 484 | 0.48 |
| Barium Oxide | 24.0 | 1.64 | 435 | 0.45 |
| Aluminum Oxide | 24.0 | 1.48 | 398 | 0.46 |
| Zirconium Oxide | 25.0 | 1.65 | 409 | 0.48 |
| Copper II Oxide | 30.0 | 1.88 | 392 | 0.54 |

Table 5.2(b)

| 5W30 Oil Immersion Results | | | | | |
|-----------------------------------------------------------------|------------------------|---------------------------|-------------|-----------------------------------|----------------|
| (1) Samples containing a Metal AcAc and CaO (Form.(B)) | | | | | |
| Additive | Durometer (Shore A) | Tensile N/mm ² | Elongation% | 100% Modulus N/mm ² | Volume Swell % |
| Chromium III AcAc | 0 | 0.60 | 829 | 0.12 | 56 |
| Iron III AcAc | 3 | 0.92 | 539 | 0.23 | 50 |
| Aluminum AcAc | 0 | 0.40 | 705 | 0.11 | 50 |
| Zirconium AcAc | 5 | 0.81 | 382 | 0.24 | 45 |
| Zinc AcAc Hydrate | 4 | 0.72 | 583 | 0.19 | 54 |
| Titanium IV Oxide AcAc | 4 | 0.76 | 446 | 0.23 | 50 |
| (2) Samples containing Copper AcAc and a Metal Oxide (Form.(A)) | | | | | |
| Additive | Durometer (Shore A) | Tensile N/mm ² | Elongation% | 100% Modulus N/mm ² | Volume Swell % |
| Zinc Oxide | 0 | 0.46 | 789 | 0.12 | 56 |
| Magnesium Oxide | 4 | 0.78 | 632 | 0.18 | 52 |
| Titanium Dioxide | 1 | 0.59 | 807 | 0.12 | 50 |
| Barium Oxide | 0 | 0.54 | 715 | 0.12 | 53 |
| Aluminum Oxide | 0 | 0.43 | 610 | 0.12 | 51 |
| Zirconium Oxide | 1 | 0.51 | 706 | 0.12 | 51 |
| Copper II Oxide | 1 | 0.53 | 632 | 0.13 | 52 |

Claims

1. A RTV silicone composition which is curable in the presence of moisture, comprising:

(A) 100 parts by weight of a polydiorganosiloxane in which the terminal groups are selected from silanol and triorganosilyl groups, provided at least 60 mole percent of the terminal groups are silanol groups;

(B) 1 to 15 parts by weight of an acyloxy-functional crosslinking agent described by the formula $R_mSi(OCOR')_4$, where R is a monovalent hydrocarbon radical selected from 1 to 12 carbon atoms, each R' is an independently selected monovalent hydrocarbon radical from 1 to 12 carbon atoms and m is 0 or 1;

(C) 0.001 to 1 part by weight of a metal salt of a carboxylic acid catalyst;

(D) 5 to 150 parts by weight of a filler; and

(E) an effective amount of a metal acetylacetonate.

2. The RTV silicone composition of claim 1 comprising 0.01 to 5 parts by weight of the metal acetylacetonate based on 100 parts by weight of the polydiorganosiloxane, where the metal portion of the metal acetylacetonate is selected from copper, chromium, iron, aluminum, zinc, titanium and zirconium.

3. The RTV silicone composition of claim 1 where the polydiorganosiloxane is a polydimethylsiloxane in which 80 to 100 mole percent of the terminal groups are silanol groups; R and R' of the acyloxy-functional crosslinking agent are independently selected from methyl and ethyl, and m is 1; the catalyst is a tin salt of a carboxylic acid and the filler is a silica filler.

4. The RTV silicone composition of claim 1 further comprising (F) 0.01 to 10 parts by weight of a metal oxide, based

on 100 parts by weight of the polydiorganosiloxane.

5. The RTV silicone composition of claim 4 comprising 0.01 to 1.5 parts by weight of the metal oxide based on 100 parts by weight of the polydiorganosiloxane, where the metal portion of the metal oxide is selected from the group consisting of calcium, zinc, magnesium, aluminum, zirconium, barium, titanium, strontium and copper.

6. A method of sealing, comprising the steps of:

(i) providing at least two substrates having a plurality of surfaces;

(ii) applying a layer of a RTV silicone composition which is curable in the presence of moisture, to at least a portion of at least one of the surfaces of at least one of the substrates, the RTV silicone composition comprising:

(A) 100 parts by weight of a polydiorganosiloxane in which the terminal groups are selected from silanol and triorganosilyl groups, provided at least 60 mole percent of the terminal groups are silanol groups,

(B) 1 to 15 parts by weight of an acyloxy-functional crosslinking agent described by the formula $R_mSi(OCOR')_{4-m}$ where R is a monovalent hydrocarbon radical selected from 1 to 12 carbon atoms, each R' is an independently selected monovalent hydrocarbon radical from 1 to 12 carbon atoms and m is 0 or 1,

(C) 0.001 to 1 part by weight of a metal salt of a carboxylic acid catalyst,

(D) 5 to 150 parts by weight of a filler, and

(E) an effective amount of a metal acetyl-acetonate,

(iii) bringing at least two of the substrates, where at least one of the substrates has the RTV silicone composition applied thereto, into proximity so as to form a gasket of the RTV silicone composition therebetween; and

(iv) exposing the gasket of step (iii) to moisture to effect curing of the RTV silicone composition.

7. The method of claim 6 where the RTV silicone composition comprises about 0.01 to 5 parts by weight of the metal acetylacetonate based on 100 parts by weight of the polydiorganosiloxane, where the metal portion of the metal acetylacetonate is selected from copper, chromium, iron, aluminum, zinc, titanium and zirconium.

8. The method of claim 6 where in the RTV silicone composition, the polydiorganosiloxane is a polydimethylsiloxane in which 80 to 100 mole percent of the terminal groups are silanol groups; R and R' of the acyloxy-functional crosslinking agent are independently selected from methyl and ethyl and m is 1; the catalyst is a tin salt of a carboxylic acid; and the filler is a silica filler.

9. The method of claim 6 where the RTV silicone composition further comprises (F) 0.01 to 10 parts by weight of a metal oxide, based on 100 parts by weight of the polydiorganosiloxane.

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 866 099 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
03.02.1999 Bulletin 1999/05

(51) Int. Cl.⁶: **C08L 83/04**

(43) Date of publication A2:
23.09.1998 Bulletin 1998/39

(21) Application number: **98105081.8**

(22) Date of filing: **20.03.1998**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **21.03.1997 US 41340 P**
10.06.1997 US 872518

(71) Applicant:
DOW CORNING CORPORATION
Midland, Michigan 48686-0994 (US)

(72) Inventors:
• **Beljanski, Philip David**
Midland, Michigan 48640 (US)
• **Lower, Loren Dale**
Midland, Michigan 48642 (US)

(74) Representative:
Spott, Gottfried, Dr. et al
Patentanwälte
Spott, Weinmiller & Partner
Sendlinger-Tor-Platz 11
80336 München (DE)

(54) **Oil resistant silicone sealants**

(57) The invention relates to a RTV silicone composition having increased hot oil resistance upon curing. The RTV silicone composition comprises a polydiorganosiloxane, an acyloxy-functional crosslinker, a metal salt of a carboxylic acid catalyst, a filler, and a metal acetylacetonate. In a preferred embodiment a metal oxide is also added.

EP 0 866 099 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 10 5081

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| The present search report has been drawn up for all claims | | | |
| Place of search BERLIN | | Date of completion of the search 4 December 1998 | Examiner Hoepfner, W |
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 10 5081

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